

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to Vinylaromatic Polymer Preparation

We, KONINKLIJKE INDUSTRIEEL MAATSCHAPPIJ NOURY & VAN DER LANDE N.V., of 13, Brink, Deventer, (The Netherlands), a company organised under the laws of The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the preparation of polymers from vinylaromatic monomers.

It is known that vinylaromatic monomers, such as styrene, α -methylstyrene, vinyltoluene, vinylcarbazole and mixtures of these compounds, may be polymerized at temperatures from 70° to 200°C. in the presence of polymerisation initiators in the form of organic peroxides, especially diacylperoxides, such as benzoylperoxide, dialkyl peroxides such as ditertiary butylperoxide and peresters such as tertiary-butylperacetate and tertiary-butylperbenzoate.

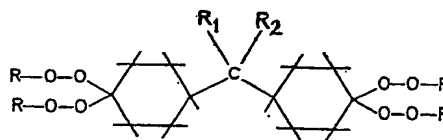
The average molecular weight of the polymers obtained depends upon the rate of polymerisation. The latter is determined to a large extent by:

(a) the nature and the concentration of the peroxidic initiator and

(b) the temperature at which the polymerisation takes place. As a general rule, the average molecular weight of the polymers is inversely proportional to the rate of polymerisation. An increase in the rate of polymerisation, e.g. by increasing the polymerisation temperature, leads to a decrease in molecular weight. Therefore, in the peroxidic polymerisation of styrene, it is necessary, as far as the polymerisation temperature is concerned, to keep to a maximum, because of the requirements, in practice, as to average molecular weight.

It has surprisingly been found that, by using peroxides of the general formula

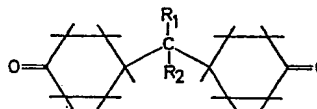
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in which R represents a tertiary alkyl or tertiary aralkyl radical and R₁ and R₂ each represent an alkyl radical with 1 or 2 carbon atoms in the preparation of polymers from vinylaromatic monomers, preferably using polymerisation temperatures between 70° and 200°C., not only are higher rates of polymerisation obtained than by using the peroxides hitherto employed under the same conditions, but also the polymers obtained have higher average molecular weights.

It has also been found that, in the polymerisation of vinylaromatic monomers to form polymers having the same average molecular weight by using peroxides according to the present invention on the one hand and peroxides hitherto employed for this purpose on the other hand, the polymers obtained with the aid of the peroxides according to the invention are qualitatively better. This may be demonstrated in a higher impact strength, a higher melt index and a lower residual styrene content of these products.

The peroxides to be used in carrying the invention into effect may be obtained by reacting a compound of the general formula



in which R₁ and R₂ have the meanings defined above, with a tertiary alkyl or tertiary

aralkyl hydroperoxide, in the presence of an acid-reacting catalyst, and eliminating from the reaction zone the water formed during the reaction.

- 5 The peroxide preparation reaction is preferably carried out in benzene at a temperature of 20°—50°C., the water formed during the reaction being eliminated by azeotropic distillation with benzene under reduced pressure.

10 The peroxides preferably used include:
 2,2 - bis(4,4 - ditertiary - butyl - peroxy-cyclohexyl) - propane,
 2,2 - bis(4,4 - ditertiary - amyl - peroxy-cyclohexyl) - propane,
 15 2,2 - bis(4,4 - dicumyl - peroxy-cyclohexyl) - propane and
 2,2 - bis(4,4 - ditertiary - butyl - peroxy-cyclohexyl) - butane.

- 20 The present invention is further illustrated by the following Examples. Where intrinsic viscosity (η) is mentioned in these Examples, it means the viscosity as stated in Allen: "Characterization of Polymers" (Butterworth, London 1959) page 173. It is expressed in 1/g and is measured at 25°C. in toluene as a solvent.

The average molecular weights are calculated according to the formula

30
$$\bar{M}_v = 2.88 \times 10^6 \times (\eta)^{1.247}$$

(see J. W. Breitenbach, "Monatshefte für Chemie", 159 (1950) 455).

EXAMPLE 1.

- 35 A mixture of 118 g (0.5 mole) of 2,2-bis(4-keto - cyclohexyl) - propane, 281 g (3 moles) of tertiary - butyl - hydroperoxide and 0.8 ml of H₂SO₄ (70% by weight) in 600 ml of benzene was heated at a temperature of 40°C.

The water formed during the reaction was eliminated by azeotropic distillation with benzene under reduced pressure. During the distillation of the water, the benzene was returned to the reaction mixture. This process was continued for 2 hours, a maximum final pot temperature of 40°C.

45 Subsequently, the reaction mixture was freed from acid by treatment with 100 ml. of sodium bicarbonate solution (5% by weight of sodium bicarbonate in water) and subsequently twice with 250 ml. of water. Thereafter, in order to eliminate the volatile constituents, it was evaporated *in vacuo* at a temperature of 40°C. 280 g. of crude peroxide in solid form were obtained. This product was taken up in a mixture of 420 ml. of ether and 980 ml. of ethanol and this solution was then allowed to crystallize by cooling to 0°C.

After filtration, 288 g. of a white crystalline 2,2 - bis(4,4 - ditertiary - butyl - peroxy-cyclohexyl) - propane was obtained, namely a yield of 81% calculated on the 2,2 - bis(4-ketocyclohexyl)-propane.

O content	11.30%	(theor. 11.43%)	
C	66.21%	(theor. 66.43%)	
H	10.38%	(theor. 10.71%)	65

This peroxide was then compared as a polymerisation initiator with equal parts by weight of benzoylperoxide, tertiary-butylperbenzoate and tertiary-butylperacetate. For this, 100 parts by weight of inhibitor-free styrene and 0.2 parts by weight of peroxide were introduced into a glass reaction vessel. After removal of atmospheric oxygen, the reaction vessel was closed and heated to a temperature of 110°C. The results obtained are given in the following table.

	Peroxide	Reaction time in hours	% conversion of styrene	(η)	\overline{M}_v
<i>a</i> . . .	2,2-bis(4,4-ditertiary-butyl-peroxycyclohexyl)-propane	1½	55.4	0.095	153,000
<i>b</i> . . .	„	2	81.5	0.119	205,000
<i>c</i> . . .	„	3½	97.8	0.132	230,000
<i>d</i> . . .	dibenzoylperoxide	2	48.5	0.078	120,000
<i>e</i> . . .	„	6	72.0	0.086	136,000
<i>f</i> . . .	tertiary-butylperbenzoate	2	40.9	0.078	120,000
<i>g</i> . . .	„	6	99.5	0.115	190,000
<i>h</i> . . .	tertiary-butylperacetate	2	52.5	0.068	102,000
<i>i</i> . . .	„	6	99.4	0.097	157,000

It appears from experiments *a*, *d*, *f* and *h* that under the prevailing circumstances 2,2-bis(4,4 - ditertiarybutyl - peroxycyclohexyl)-propane, in comparison with the other peroxides mentioned in the table, causes the most rapid polymerisation.

It appears from experiments *a* and *h* that the use of a peroxide according to the invention, notwithstanding the higher rate of polymerisation at almost the same conversion degree, a higher molecular weight is obtained. This also appears from experiments *c*, *g* and

i, in which the polymerisation was almost complete.

EXAMPLE 2.

2,2 - bis(4,4 - ditertiary - butyl - peroxy-cyclohexyl)-propane, prepared in the manner as described in Example 1, was compared as a polymerisation initiator for styrene with tertiary-butylperacetate.

The polymerisation reaction conditions such as the peroxide percentage by weight used, the polymerisation temperature and time and the results obtained are given in the following table:

Peroxide	% by weight peroxide	temp. °C.	reaction time in hours	% conversion of styrene	(η)	\overline{M}_v
2,2-bis(4,4-ditert. butyl-peroxy-cyclohexyl)propane	0.20	110	3	99.6	0.110	185,000
„	0.15	110	5	100.0	0.122	210,000
„	0.10	110	5	98.8	0.132	230,000
„	0.20	120	2	97.3	0.107	180,000
„	0.20	130	1.5	87.4	0.091	145,000
„	0.20	100	6	98.7	0.162	295,000
tert. butyl-peracetate	0.20	110	5	100.0	0.075	115,000
„	0.20	100	6	94.2	0.138	245,000
„	0.10	100	6	60.9	0.127	220,000

EXAMPLE 3.

Into an autoclave from which the air had been removed by means of nitrogen, there were introduced successively:

- 5 200 parts by weight of distilled water;
 0.3 parts by weight of a polyvinyl alcohol (marketed by E. I. Du Pont de Nemours under the trade name ELVANOL 50-42);
 10 100 parts by weight of inhibitor-free styrene;
 0.2 parts by weight of 2,2-bis(4,4-ditertiary-butyl-peroxycyclohexyl)-propane obtained as described in Example 1.

After a reaction time of 4 hours at 110°C., complete conversion was obtained. The intrinsic viscosity (η) and the molecular weight \bar{M}_v were 0.136 and 240,000 respectively.

After polymerisation for 6 hours under otherwise similar conditions, using 0.2 parts by weight of tertiary-butyl-peracetate, instead of 2,2-bis(4,4-ditertiary-butyl-peroxycyclohexyl)-propane, a completely polymerised product was obtained, the intrinsic viscosity (η) and the molecular weight \bar{M}_v of which were 0.099 and 160,000 respectively.

EXAMPLE 4.

In the way as described in Example 3, 100 parts by weight of styrene were polymerised with 0.4 parts by weight of 2,2-bis(4,4-ditertiary-butyl-peroxy-cyclohexyl)-propane and an equal quantity of styrene was polymerised with 0.2 parts by weight of tertiary-butyl-peracetate to polymers with about the same molecular weight.

The results obtained are given in the following table:

Peroxide	(η)	\bar{M}_v	Impact strength Kg/cm/cm ²	Melt-index	Residual styrene content in % by weight
2,2-bis(4,4-ditert. butyl-peroxy-cyclohexyl)-propane	0.100	163,000	7.3	0.26	0.00
tert. butyl-peracetate	0.103	168,000	6.1	0.19	0.20

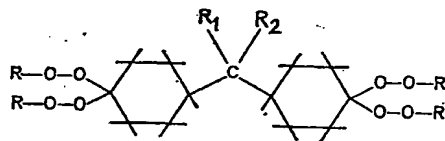
40 The impact strength was determined according to the ASTM-0256 method Charpy, not notched.

The melt index was executed according to B.S. 2782 (part 1-1956) at a temperature of 190°C.

45 In carrying the invention into effect, the polymerisation reaction is preferably effected at a temperature of 100° to 130°C., as illustrated by the above Examples. The amount of peroxidic initiator used is preferably in the range of 0.05-1.00% by weight, based upon the initial monomer.

WHAT WE CLAIM IS:—

55 1. A process for the peroxidic polymerisation of vinylaromatic monomers, in which a compound is used as initiator having the general formula:



60 in which R represents a tertiary alkyl or tertiary aralkyl radical and R_1 and R_2 each repre-

sent an alkyl radical with 1 or 2 carbon atoms.

2. A process according to claim 1, in which the initiator is 2,2-bis(4,4-ditertiary-butyl-peroxy-cyclohexyl)-propane.

3. A process according to claim 1 or 2, in which styrene is used as a monomer.

4. A process according to any preceding claim, in which the initiator is used in a concentration of 0.05-1.00% by weight calculated on the starting monomer.

5. A process according to any preceding claim, in which the polymerisation is carried out at a temperature from 70° to 200°C.

6. A process according to claim 5, in which the temperature is from 100° to 130°C.

7. A process for the peroxidic polymerisation of vinyl-aromatic monomers according to claim 1, as described with reference to the foregoing Examples.

8. A vinylaromatic polymer, when prepared by a process according to any preceding claim.

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